

CLAIMS

1. An emulsion polymerisation process comprising the following steps:

- a) providing a mixture of ethylenically unsaturated monomers including water insoluble monomer;
- b) dispersing the mixture of ethylenically unsaturated monomers into an aqueous liquid to form an oil-in-water emulsion;
- c) adding to the oil-in-water emulsion an ammonium phosphate ester zwitterionic monomer;
- d) adding a water-soluble radical initiator to the oil-in water emulsion;
- e) polymerising the monomers to form a product latex of polymer having a polymer solids concentration in the product of at least 20% by weight.

2. An emulsion polymerisation process according to claim 1 in which the solids concentration of the product is up to 60%.

3. An emulsion polymerisation process according to claim 2 in which the solids concentration of the product is in the range 25 to 50%.

4. An emulsion polymerisation process according to claim 1 in which the oil-in-water emulsion is substantially free of non-polymerisable surfactants.

5. An emulsion polymerisation process according to claim 1 in which the ammonium phosphate ester zwitterionic monomer is included in the process in an amount in the range 0.01 to 5% by weight based on the total weight of monomers.

6. An emulsion polymerisation process according to claim 5 in which the said amount is in the range 0.05 to 2% by weight.

7. An emulsion polymerisation process according to any preceding claim in which the ammonium phosphate ester zwitterionic monomer has the general formula I

YBX

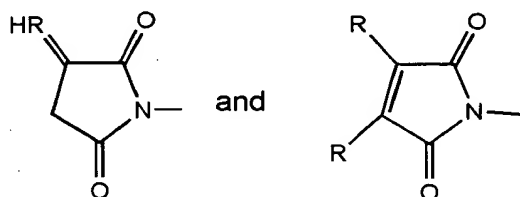
I

in which X is said ammonium phosphate ester zwitterionic group;

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B is selected from the group consisting of a bond, and straight and branched alkanediyl, alkylene oxaalkylene, and alkylene (oligooxaalkylene) groups, optionally containing one or more fluorine substituents; and

Y is an ethylenically unsaturated group selected from the group consisting of $\text{H}_2\text{C}=\text{CR}-\text{CO}-\text{A}-$, $\text{H}_2\text{C}=\text{CR}-\text{C}_6\text{H}_4-\text{A}^1-$, $\text{H}_2\text{C}=\text{CR}-\text{CH}_2\text{A}^2-$, $\text{R}^2\text{O}-\text{CO}-\text{CR}=\text{CR}-\text{CO}-\text{O}-$, $\text{RCH}=\text{CH}-\text{CO}-\text{O}-$, $\text{RCH}=\text{C}(\text{COOR}^2)\text{CH}_2-\text{CO}-\text{O}-$,



A is $-\text{O}-$ or NR^1 ;

15 A^1 is selected from the group consisting of a bond, $(\text{CH}_2)_n\text{A}^2$ and $(\text{CH}_2)_n\text{SO}_3^-$ in which n is 1 to 12;

A^2 is selected from the group consisting of a bond, $-\text{O}-$, $\text{O}-\text{CO}-$, $-\text{CO}-\text{O}$, $-\text{CO}-\text{NR}^1-$, $-\text{NR}^1-\text{CO}$, $-\text{O}-\text{CO}-\text{NR}^1-$, and $-\text{NR}^1-\text{CO}-\text{O}-$;

R is hydrogen or C_{1-4} alkyl;

20 R^1 is selected from the group consisting of hydrogen, C_{1-4} alkyl and BX ; and

R^2 is hydrogen or C_{1-4} alkyl.

8. An emulsion polymerisation process according to claim 1 in which the monomers include at least 50% by weight based on total ethyleneically unsaturated monomers of a hydrophobic ethylenically unsaturated polymerisable compound.

9. An emulsion polymerisation process according to claim 8 in which the said hydrophobic compound is selected from the group consisting of C_{1-12} alkyl(alk)acrylates and C_{2-12} -alkyl and -dialkyl(alk)acrylamides, styrene, and mixtures thereof.

30 10. An emulsion polymerisation process according to claim 1 comprising further adding to the oil-in-water emulsion a sulfo- or carboxy-betaine monomer.

11. An emulsion polymerisation process according to claim 10 in which the weight ratio of betaine monomer to ammonium phosphate ester zwitterionic monomer is in the range (1-50):1.

12. An emulsion polymerisation process according to claim 11 in which the said ratio is in the range (5-20):1.

13. An emulsion polymerisation process according to claim 1 comprising adding to the oil-in-water emulsion a hydrophilic monomer.

14. An emulsion polymerisation process according to claim 13 in which the hydrophilic monomer is selected from the group consisting of C₂₋₄-hydroxyalkyl(meth)acrylates, C₁₋₄-hydroxyalkyl(meth)acrylamides, C₁₋₃-alkoxy-C₂₋₄-alkyl(meth)acrylates, C₁₋₃-alkoxy-C₂₋₄-alkyl(meth)acrylamides, C₁₋₃-alkoxy-oligoethoxy(meth)acrylates, C₁₋₄-dihydroxyalkyl(meth)acrylates, N-mono- and N,N-di-C₁₋₂ alkyl(meth)acrylamides, N-vinylactams and C₂₋₄ hydroxyalkyl oligoethoxy(meth)acrylates, and mixtures thereof.

15. An emulsion polymerisation process according to claim 13 in which the said hydrophilic monomer is added in an amount in the range 0.1 to 50% by weight, based on the total weight of monomer.

16. A process according to claim 15 in which the said range is 5 to 20% by weight.

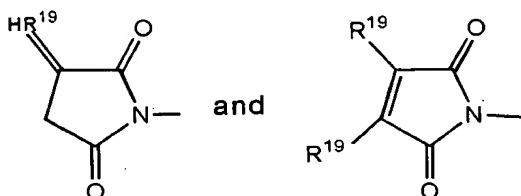
17. An emulsion polymerisation process according to claim 1 comprising adding to the oil-in-water emulsion an acidic monomer in an amount to confer an acidic pH on the oil-in-water emulsion.

18. An emulsion polymerisation process according to claim 17 in which the acidic monomer is acrylic acid or methacrylic acid, and it is present in an amount in the range 0.1 to 5% by weight based on the total weight of monomers.

19. An emulsion polymerisation process according to claim 1 comprising adding to the oil-in-water emulsion a cationic monomer, of the general formula VIII

in which Y^2 is an ethylenically unsaturated group selected from the group consisting of $H_2C=CR^{19}-CO-A^8$ -, $H_2C=CR^{19}-C_6H_4-A^9$ -, $H_2C=CR^{19}-CH_2A^{10}$ -, $R^{21}O-CO-CR^{19}=CR^{19}-CO-O$ -, $R^{19}CH=CH-CO-O$ -, $R^{19}CH=C(COOR^{21})CH_2-CO-O$ -,

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A^8 is $-O-$ or $-NR^{20}-$;

A^9 is selected from the group consisting of a bond, $(CH_2)_qA^{10}$ and $(CH_2)_qSO_3-$ in which q is 1 to 12;

A^{10} is selected from the group consisting of a bond, $-O-$, $O-CO-$, $-CO-O$, $-CO-NR^{20}-$, $-NR^{20}-CO$, $O-CO-NR^{20}-$, and $NR^{20}-CO-O$;

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R^{19} is hydrogen or C_{1-4} alkyl;

R^{20} is selected from the group consisting of hydrogen, C_{1-4} alkyl and BX ;

R^{21} is hydrogen or C_{1-4} alkyl;

20

B^2 is selected from the group consisting of a bond, and straight and branched alkanediyl, alkylene oxaalkylene, and alkylene (oligooxalkylene) group, optionally containing one or more fluorine substituents; and

Q is selected from the group consisting of $-N^*R^{22}_3$, $-P^*R^{23}_3$ and $-S^*R^{23}_2$ in which the groups R^{22} are the same or different and each is selected from the group consisting of hydrogen, alkyl of 1 to 6 carbon atoms, C_{1-6}

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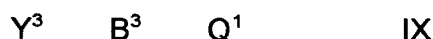
hydroxyalkyl, aryl, and C_{7-12} aralkyl, or two of the groups R^{22} together with the nitrogen atom to which they are attached form an aliphatic heterocyclic ring containing from 5 to 7 atoms, or the three groups R^{22} together with the nitrogen atom to which they are attached form a fused ring structure containing from 5 to 7 atoms in each ring, and optionally one or more of the groups R^{22} is substituted by a hydrophilic functional group, and

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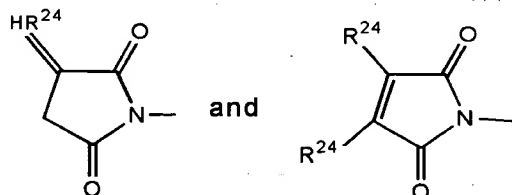
the groups R^{23} are the same or different and each is R^{22} or a group OR^{22} , where R^{22} is as defined above *mutatis mutandis*.

20. An emulsion polymerisation process according to claim 19 in which Y^2 is $H_2C=CR^{19}COA-$, in which R^{12} is hydrogen or methyl and A is -O- or -NH-, B^2 is straight chain C_{2-6} alkanediyl group and Q is $-N^eR^{22}_3$ where each R^{22} group is a C_{1-4} alkyl group.

21. An emulsion polymerisation process according to claim 1 comprising further adding to the oil-in-water emulsion a reactive monomer having the general formula IX



in which Y^3 is an ethylenically unsaturated group selected from the group consisting of $H_2C=CR^{24}-CO-A^{11}-$, $H_2C=CR^{24}-C_6H_4-A^{12}-$, $H_2C=CR^{19}-CH_2A^{13}$, $R^{26}O-CO-CR^{24}=CR-CO-O-$, $R^{24}CH=CH-CO-O-$, $R^{24}CH=C(COOR^{26})CH_2-CO-O-$,



A^{11} is -O- or $-NR^{25}$;

A^{12} is selected from the group consisting of a bond, $(CH_2)_rA^{13}$ and $(CH_2)_rSO_3-$ in which r is 1 to 12;

A^{13} is selected from the group consisting of a bond, -O-, O-CO-, CO-O-, -CO- NR^{25} -, $-NR^{25}$ -CO-, -O-CO- NR^{25} -, and NR^{25} -CO-O-;

R^{24} is hydrogen or C_{1-4} alkyl;

R^{25} is selected from the group consisting of hydrogen, C_{1-4} alkyl and B^3Q^1 ;

R^{26} is hydrogen or C_{1-4} alkyl;

B^3 is selected from the group consisting of a bond, straight and branched alkanediyl, alkylene oxaalkylene, and alkylene (oligooxaalkylene) groups, optionally containing one or more fluorine substituents.

Q^1 is a reactive group selected from the group consisting of aldehyde groups; silane and siloxane groups containing one or more substituents selected from halogen atoms and C_{1-4} -alkoxy groups; hydroxyl; amino;

carboxyl; epoxy; $-\text{CHOHCH}_2\text{Hal}$ (in which Hal is selected from chlorine, bromine and iodine atoms); succinimido; tosylate; triflate; imidazole carbonyl amino; optionally substituted triazine groups; cinnamyl; ethylenically and acetylenically unsaturated groups; acetoacetoxy; methylol; and
 5 chloroalkylsulphone groups; acetoxy; mesylate; carbonyl di(cycloalkyl carbodiimidoyl; and oximino.

22. An emulsion polymerisation process according to claim 21 in which Y^3 is $\text{H}_2\text{C}=\text{CR}^{24}\text{COA}^-$ in which R^{24} is hydrogen or methyl and A^- is $-\text{O}-$ or $\text{NH}-$, B^3 is a straight chain C_{2-6} -alkanediyl group; and Q^1 is a
 10 trimethoxysilyl group.

23. An emulsion polymerisation process according to claim 22 in which the monomers include a hydrophilic monomer selected from the group consisting of C_{2-4} hydroxyalkyl(alk)acrylates and mono- or di- C_{2-4} hydroxyalkyl(alk)acrylamides.

15 24. An emulsion polymerisation process comprising the following steps:

- i) adding an ethylenically unsaturated ammonium phosphate ester zwitterionic monomer and a water-soluble radical initiator in a first stage to an aqueous liquid to form an aqueous continuous phase;
- 20 ii) forming a monomer seed mixture comprising water-insoluble ethylenically unsaturated monomer, and water-soluble ethylenically unsaturated monomer;
- iii) before, simultaneously or after step i) adding the monomer seed mixture to the aqueous continuous phase to form a water-in-oil
 25 emulsion;
- iv) after both steps i) and iii) adding water-soluble initiator and initiating polymerisation to form an oil-in-water dispersion of emulsion-polymerised polymer seeds;
- v) forming a seed growth monomer mixture comprising water-
 30 insoluble ethylenically unsaturated monomer;
- vi) dispersing the seed growth monomer to the dispersion of emulsion-polymerised seeds to form an oil-in-water seed growth emulsion;

vii) adding seed growth initiator to the seed growth emulsion and initiating seed growth polymerisation in the seed growth emulsion to form a product latex.

25. An emulsion polymerisation process according to claim 24 in which the composition of the combination of monomer seed mixture and zwitterionic monomer is different to the composition of the seed growth monomer mixture.

26. An emulsion polymerisation process according to claim 25 in which the monomer seed mixture consists substantially only of hydrophobic ethylenically unsaturated monomer.

27. An emulsion polymerisation process according to claim 26 in which the hydrophobic monomer is selected from the group consisting of C₁₋₁₂ alkyl(alk)acrylates and C₂₋₁₂-alkyl and di-alkyl(ak)acrylamides, styrene, and mixtures thereof.

28. An emulsion polymerisation process according to claim 25 in which the seed growth monomer mixture comprises ethylenically unsaturated ammonium phosphate ester zwitterionic monomer.

29. An emulsion polymerisation process according to claim 28 in which seed growth monomer mixture comprises water-soluble ethylenically unsaturated monomers.

30. An emulsion polymerisation process according to claim 29 in which the said water-soluble monomers comprise a hydrophilic monomer.

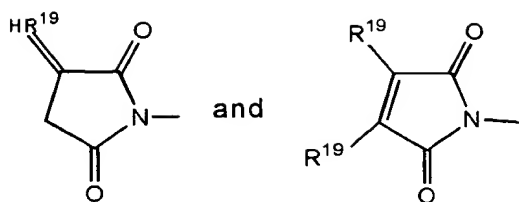
31. A process according to claim 29 in which the said water soluble monomers include acrylic or methacrylic acid.

32. An emulsion polymerisation process according to claim 29 in which the said water-soluble monomers include a cationic monomer, of the general formula VIII



in which Y² is an ethylenically unsaturated group selected from the group consisting of H₂C=CR¹⁹-CO-A⁸-, H₂C=CR¹⁹-C₆H₄-A⁹-, H₂C=CR¹⁹-CH₂A¹⁰-, R²¹O-CO-CR¹⁹=CR¹⁹-CO-O-, R¹⁹CH=CH-CO-O-, R¹⁹CH=C(COOR²¹)CH₂-CO-O-,

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A^8 is -O- or -NR²⁰-;

A^9 is selected from the group consisting of a bond, (CH₂)_qA¹⁰ and (CH₂)_q SO₃⁻ in which q is 1 to 12;

A^{10} is selected from the group consisting of a bond, -O-, O-CO-, -CO-O-, -CO-NR²⁰-, -NR²⁰-CO-, O-CO-NR²⁰-, and NR²⁰-CO-O-;

R¹⁹ is hydrogen or C₁₋₄ alkyl;

R²⁰ is selected from the group consisting of hydrogen, C₁₋₄ alkyl and BX;

R²¹ is hydrogen or C₁₋₄ alkyl;

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B² is selected from the group consisting of a bond, and straight and branched alkanediyl, alkylene oxaalkylene, and alkylene (oligooxalkylene) group, optionally containing one or more fluorine substituents; and

Q is selected from the group consisting of -N⁺R²²₃, -P⁺R²³₃ and -S⁺R²³₂, in which the groups R²² are the same or different and each is selected from the group consisting of hydrogen, alkyl of 1 to 6 carbon atoms, C₁₋₆ hydroxyalkyl, aryl, and C₇₋₁₂ aralkyl, or two of the groups R²² together with the nitrogen atom to which they are attached form an aliphatic heterocyclic ring containing from 5 to 7 atoms, or the three groups R²² together with the nitrogen atom to which they are attached form a fused ring structure containing from 5 to 7 atoms in each ring, and optionally one or more of the groups R²² is substituted by a hydrophilic functional group, and

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the groups R²³ are the same or different and each is R²² or a group OR²², where R²² is as defined above *mutatis mutandis*.

33. An emulsion polymerisation process according to claim 32 in which Y² is H₂C=CR¹⁹COA-, in which R¹² is hydrogen or methyl and A is -O- or -NH-, B² is straight chain C₂₋₆ alkanediyl group and Q is -N⁺R²²₃ where each R²² group is a C₁₋₄ alkyl group.

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34. An emulsion polymerisation process according to claim 24 in which at least a portion of seed growth monomers are premixed before being added to the continuous phase in step iv.

5 35. An emulsion polymerisation process according to claim 34 in which the seed growth monomer mixture is continuously fed into the oil-in-water dispersion compositions of emulsion-polymerised seeds over a monomer feed period during which polymerisation continues.

10 36. An emulsion polymerisation process according to claim 35 comprising providing an initiator feed comprising the seed growth initiator and continuously feeding the initiator feed, into the oil-in-water dispersion comprising emulsion polymerised seeds throughout the monomer feed period.

15 37. An emulsion polymerisation process according to claim 35 in which a portion of initiator feed is added to the polymerised growth polymerisation mixture after all the premixed seed growth monomer mixture has been added under conditions such that radicals are formed from the initiator.

20 38. An emulsion polymerisation process according to claim 36 in which the initiator feed comprises water-soluble monomer.

20 39. An emulsion polymerisation process according to claim 38 in which the water-soluble monomer comprises a sulfo- or carboxy-betaine monomer.

25 40. An emulsion polymerisation process according to claim 24 in which the latex product comprises a stable dispersion of polymer particles, having a polymer concentration in the range 20 to 60% by weight.

41. An emulsion polymerisation process according to claim 24 in which the latex product comprises a dispersed phase having a particle diameter less than 1 μ m.

30 42. An emulsion polymerisation according to claim 41 in which the particle diameter is in the range 100 to 400 μ m.

43. A stable of polymer particles in an aqueous continuous phase, having a polymer concentration in the range 20 to 60% by weight, based on

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total weight of dispersion, an average particle diameter of less than $1\mu\text{m}$, the polymer being formed from radical polymerised ethylenically unsaturated monomers comprising water-insoluble monomer and ammonium phosphate ester zwitterionic monomer.

5 44. A latex according to claim 43 further comprising suspended particulate solids selected from organic and inorganic water-insoluble materials.

45. A latex according to claim 43 in which the ammonium phosphate ester zwitterionic monomer has the general formula I

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YBX

I

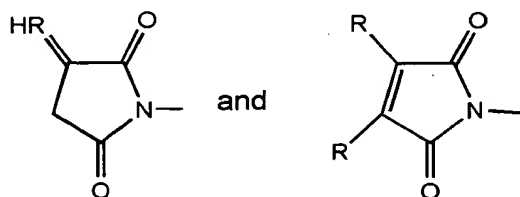
in which X is an ammonium phosphate ester zwitterionic group;

B is selected from the group consisting of a bond, and straight and branched alkanediyl, alkylene oxaalkylene, and alkylene (oligooxalkylene) groups, optionally containing one or more fluorine substituents; and

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Y is an ethylenically unsaturated group selected from the group consisting of $\text{H}_2\text{C}=\text{CR}-\text{CO}-\text{A}-$, $\text{H}_2\text{C}=\text{CR}-\text{C}_6\text{H}_4-\text{A}^1-$, $\text{H}_2\text{C}=\text{CR}-\text{CH}_2\text{A}^2-$, $\text{R}^2\text{O}-\text{CO}-\text{CR}=\text{CR}-\text{CO}-\text{O}-$, $\text{RCH}=\text{CH}-\text{CO}-\text{O}-$, $\text{RCH}=\text{C}(\text{COOR}^2)\text{CH}_2-\text{CO}-\text{O}-$,

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A is $-\text{O}-$ or NR^1 ;

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A^1 is selected from the group consisting of a bond, $(\text{CH}_2)_n\text{A}^2$ and $(\text{CH}_2)_n\text{SO}_3-$ in which n is 1 to 12;

A^2 is selected from the group consisting of a bond, $-\text{O}-$, $\text{O}-\text{CO}-$, $-\text{CO}-\text{O}$, $-\text{CO}-\text{NR}^1-$, $-\text{NR}^1-\text{CO}$, $-\text{O}-\text{CO}-\text{NR}^1-$, and $-\text{NR}^1-\text{CO}-\text{O}-$;

R is hydrogen or C_{1-4} alkyl;

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R^1 is selected from the group consisting of hydrogen, C_{1-4} alkyl and BX; and

R^2 is hydrogen or C_{1-4} alkyl.

46. A latex according to claim 43 in which the water-insoluble monomer comprises a hydrophobic ethylenically unsaturated monomer which is selected from the group consisting of C₁₋₁₂ alkyl(alk)acrylates and C₂₋₁₂-alkyl and di-alkyl(ak)acrylamides, styrene, and mixtures thereof.

5 47. A coating process in which a dispersion of polymer particles in an aqueous continuous phase, having a polymer concentration in the range 20 to 60% by weight, based on total weight of dispersion, an average particle diameter of less than 1 µm, the polymer being formed from radical polymerised ethylenically unsaturated monomers comprising water-insoluble monomer and ammonium phosphate ester zwitterionic monomer is coated
10 onto a substrate to form a liquid coating on a surface thereof, and water is removed from the liquid coating to form a stable solid polymer coating on the said surface.

15 48. A coating process according to claim 47 in which the water is removed by evaporation and the polymer particles coalesce during the evaporation of water to form a solid polymer film on the surface.

49. A coating process according to claim 47 in which the surface bearing the solid polymer coating is contacted with an aqueous biological liquid.

20 50. A coating process according to claim 49 in which the biological liquid is selected from blood and serum.

25 51. A biocompatibilising process in which a substrate is biocompatibilised by coating it with a dispersion of polymer particles in an aqueous continuous phase, having a polymer concentration in the range 20 to 60% by weight, based on total weight of dispersion, an average particle diameter of less than 1 µm, the polymer being formed from radical polymerised ethylenically unsaturated monomers comprising water-insoluble monomer and ammonium phosphate ester zwitterionic monomer to form a liquid coating thereon and removing the water from the liquid coating to
30 leave a stable coating of solid polymer on the surface, whereby the coated surface of the substrate has improved biocompatibility as compared to the uncoated surface.

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52. A polymer formed by radical polymerisation of ethylenically unsaturated monomers, in which the monomers comprise:

- i) 0.1 to 25 weight% of an ammonium phosphate ester zwitterionic monomer;
- 5 ii) 0.1 to 25 weight% of a zwitterionic comonomer different said ammonium phosphate ester zwitterionic monomer; and
- iii) 25 to 99% of a hydrophobic monomer.

53. A polymer according to claim 52 in which the hydrophobic monomer is selected from the group consisting of C_{1-12} alkyl(alk)acrylates and N-mono- and di- C_{2-12} -alkyl(ak)acrylamides, styrene, and mixtures thereof.

54. A polymer according to claim 52 in which the monomers further comprise

- iv) 0.01 to 50% hydrophilic monomer selected from the group consisting of C_{2-4} -hydroxyalkyl(meth)acrylates, C_{1-4} -hydroxyalkyl(meth) acrylamides, C_{1-3} -alkoxy- C_{2-4} -alkyl(meth)acrylates, C_{1-3} -alkoxy- C_{2-4} -alkyl(meth)acrylamides, C_{1-3} -alkoxy-oligoethoxy(meth)acrylates C_{1-4} - dihydroxyalkyl(meth)acrylates, N-mono- and N,N- di- C_{1-2} alkyl (meth)acrylamides, N-vinylactams and C_{2-4} hydroxyalkyl oligoethoxy(meth) acrylates, and mixtures thereof.

55. A polymer according to claim 54, in which the hydrophilic monomer comprises a C_{1-3} -alkoxy-oligoethoxy(meth)acrylate or a C_{2-4} -hydroxyalkyl-oligoethoxy(meth)acrylate.

56. A polymer according to claim 52 in which the ammonium phosphate ester zwitterionic monomer is included in an amount in the range 0.01 to 5% by weight based on the total weight of monomers.

57. A polymer according to claim 52 in which the ammonium phosphate ester zwitterionic monomer has the general formula

YBX

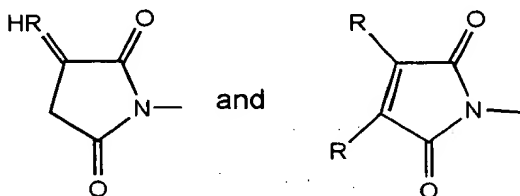
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in which X is an ammonium phosphate ester zwitterionic group;

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B is selected from the group consisting of a bond, straight and branched alkanediyl, alkylene oxaalkylene, or alkylene (oligooxalkylene) groups, optionally containing one or more fluorine substituents; and

Y is an ethylenically unsaturated group selected from the group consisting of $\text{H}_2\text{C}=\text{CR}-\text{CO}-\text{A}-$, $\text{H}_2\text{C}=\text{CR}-\text{C}_6\text{H}_4-\text{A}^1-$, $\text{H}_2\text{C}=\text{CR}-\text{CH}_2\text{A}^2-$, $\text{R}^2\text{O}-\text{CO}-\text{CR}=\text{CR}-\text{CO}-\text{O}-$, $\text{RCH}=\text{CH}-\text{CO}-\text{O}-$, $\text{RCH}=\text{C}(\text{COOR}^2)\text{CH}_2-\text{CO}-\text{O}-$,



A is $-\text{O}-$ or NR^1 ;

A^1 is selected from the group consisting of a bond, $(\text{CH}_2)_n\text{A}^2$ and $(\text{CH}_2)_n\text{SO}_3^-$ in which n is 1 to 12;

A^2 is selected from the group consisting of a bond, $-\text{O}-$, $\text{O}-\text{CO}-$, $-\text{CO}-\text{O}$, $-\text{CO}-\text{NR}^1-$, $-\text{NR}^1-\text{CO}$, $-\text{O}-\text{CO}-\text{NR}^1-$, and $-\text{NR}^1-\text{CO}-\text{O}-$;

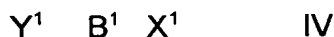
R is hydrogen or C_{1-4} alkyl;

R^1 is selected from the group consisting of hydrogen, C_{1-4} alkyl and BX; and

R^2 is hydrogen or C_{1-4} alkyl.

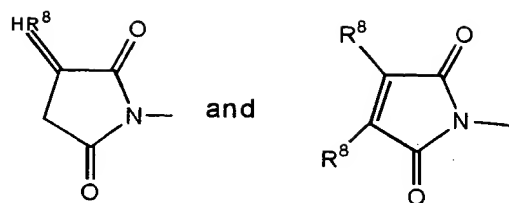
58. A polymer according to claim 52 in which the monomers include at least 50% by weight of a hydrophobic compound selected from C_{1-12} alkyl(alk)acrylates and C_{2-12} -alkyl and di-alkyl(ak)acrylamides, styrene, and mixtures thereof.

59. A polymer according to claim 52 in which the zwitterionic comonomer has the general formula IV



in which

Y^1 is an ethylenically unsaturated group selected from the group consisting of $\text{H}_2\text{C}=\text{CR}^8-\text{CO}-\text{A}^6-$, $\text{H}_2\text{C}=\text{CR}^8-\text{C}_6\text{H}_4-\text{A}^3-$, $\text{H}_2\text{C}=\text{CR}^8-\text{CH}_2\text{A}^4-$, $\text{R}^9\text{O}-\text{CO}-\text{CR}^8=\text{CR}^8-\text{CO}-\text{O}-$, $\text{R}^8\text{CH}=\text{CH}-\text{CO}-\text{O}-$, $\text{R}^8\text{CH}=\text{C}(\text{COOR}^9)\text{CH}_2-\text{CO}-\text{O}$,



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A^6 is -O- or NR^{10} ;

A^3 is selected from the group consisting of a bond, $(CH_2)_m A^4$ and $(CH_2)_m SO_3^-$ in which m is 1 to 12;

A^4 is selected from the group consisting of a bond, -O-, O-CO-, CO-O-,
10 -CO- NR^{10} -, - NR^{10} -CO-, -O-CO- NR^{10} -, and NR^{10} -CO-O-;

R^8 is hydrogen or C_{1-4} alkyl;

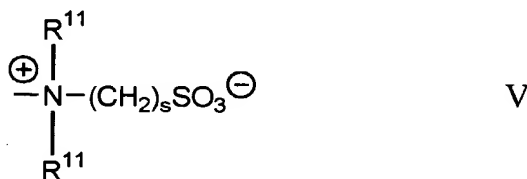
R^{10} is selected from the group consisting of hydrogen, C_{1-4} alkyl and
 $B^1 X^1$;

R^9 is hydrogen or C_{1-4} alkyl;

15 B^1 is selected from the group consisting of a bond, straight and
branched alkanediyl, alkylene oxaalkylene, or alkylene (oligooxalkylene)
groups, optionally containing one or more fluorine substituents; and

X^1 is a zwitterionic group other than an ammonium phosphate ester.

20 60. A polymer according to claim 59 in which X^1 is a group having
the general formula V

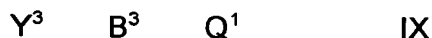


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wherein the groups R^{11} are the same or different and each is selected from
the group consisting of hydrogen and C_{1-4} alkyl groups and s is from 2 to 4.

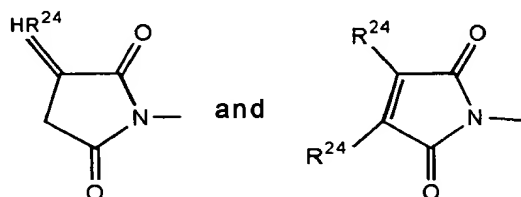
61. A polymer according to claim 52 further comprising

30 v) 0.01 to 20% by weight of a reactive monomer having the
general formula IX



in which Y^3 is an ethylenically unsaturated group selected from the group consisting of $H_2C=CR^{24}-CO-A^{11}-$, $H_2C=CR^{24}-C_6H_4-A^{12}-$, $H_2C=CR^{19}-CH_2A^{13}$, $R^{26}O-CO-CR^{24}=CR-CO-O-$, $R^{24}CH=CH-CO-O-$, $R^{24}CH=C(COOR^{26})CH_2-CO-O-$,

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A^{11} is $-O-$ or $-NR^{25}$;

A^{12} is selected from the group consisting of a bond, $(CH_2)_rA^{13}$ and $(CH_2)_rSO_3-$ in which r is 1 to 12;

A^{13} is selected from the group consisting of a bond, $-O-$, $O-CO-$, $CO-O$, $-CO-NR^{25}-$, $-NR^{25}-CO$, $-O-CO-NR^{25}-$, and $NR^{25}-CO-O-$;

15

R^{24} is hydrogen or C_{1-4} alkyl;

R^{25} is selected from the group consisting of hydrogen, C_{1-4} alkyl and B^3Q^1 ;

R^{26} is hydrogen or C_{1-4} alkyl;

20

B^3 is selected from the group consisting of a bond, straight and branched alkanediyl, alkylene oxaalkylene, and alkylene (oligooxalkylene) groups, optionally containing one or more fluorine substituents.

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Q^1 is a reactive group selected from the group consisting of aldehyde groups; silane and siloxane groups containing one or more substituents selected from halogen atoms and C_{1-4} -alkoxy groups; hydroxyl; amino; carboxyl; epoxy; $-CHOHCH_2Hal$ (in which Hal is selected from chlorine, bromine and iodine atoms); succinimido; tosylate; triflate; imidazole carbonyl amino; optionally substituted triazine groups; cinnamyl; ethylenically and acetylenically unsaturated groups; acetoacetoxyl; methylol; and chloroalkylsulphone groups; acetoxy; mesylate; carbonyl di(cycloalkyl carbodiimidoyl); and oximino.

30

62. An emulsion polymerisation process according to claim 61 in which Y^3 is $H_2C=CR^{24}COA^n-$ in which R^{24} is hydrogen or methyl and A^{11} is -

O- or NH-, B³ is a straight chain C₂₋₆-alkanediyl group; and Q¹ is a trimethoxysilyl group.

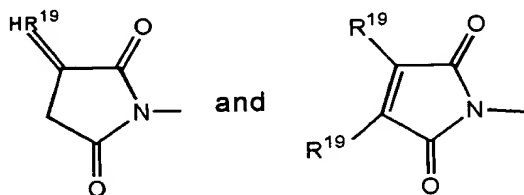
63. A emulsion polymerisation polymer according to claim 52 in which the ethylenically unsaturated monomers further comprise

- 5 vi) 0.01 to 5% by weight of an anionic monomer selected from the group consisting of fumaric acid, maleic acid, vinyl sulphonic acid, styrene sulphonic acid, acrylic acid and methacrylic acid.

64. An emulsion polymerisation polymer according to claim 52 in which the ethylenically unsaturated monomers further comprise 0.01 to 25% by weight of a cationic monomer, of the general formula VIII



in which Y² is an ethylenically unsaturated group selected from the group consisting of H₂C=CR¹⁹-CO-A⁸-, H₂C=CR¹⁹-C₆H₄-A⁹-, H₂C=CR¹⁹-CH₂A¹⁰-, R²¹O-CO-CR¹⁹=CR¹⁹-CO-O-, R¹⁹CH=CH-CO-O-,
15 R¹⁹CH=C(COOR²¹)CH₂-CO-O-,



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A⁸ is -O- or -NR²⁰-;

A⁹ is selected from the group consisting of a bond, (CH₂)_qA¹⁰ and (CH₂)_qSO₃- in which q is 1 to 12;

A¹⁰ is selected from the group consisting of a bond, -O-, O-CO-, -CO-O-, -CO-NR²⁰-, -NR²⁰-CO, O-CO-NR²⁰-, and NR²⁰-CO-O-;

R¹⁹ is hydrogen or C₁₋₄ alkyl;

R²⁰ is selected from the group consisting of hydrogen, C₁₋₄ alkyl and BX;

R²¹ is hydrogen or C₁₋₄ alkyl;

30 B² is selected from the group consisting of a bond, and straight and branched alkanediyl, alkylene oxaalkylene, and alkylene (oligooxaalkylene) group, optionally containing one or more fluorine substituents; and

Q is selected from the group consisting of $-N^+R^{22}_3$, $-P^+R^{23}_3$ and $-S^+R^{23}_2$ in which the groups R^{22} are the same or different and each is selected from the group consisting of hydrogen, alkyl of 1 to 6 carbon atoms, C_{1-6} hydroxyalkyl, aryl, and C_{7-12} aralkyl, or two of the groups R^{22} together with the nitrogen atom to which they are attached form an aliphatic heterocyclic ring containing from 5 to 7 atoms, or the three groups R^{22} together with the nitrogen atom to which they are attached form a fused ring structure containing from 5 to 7 atoms in each ring, and optionally one or more of the groups R^{22} is substituted by a hydrophilic functional group, and

the groups R^{23} are the same or different and each is R^{22} or a group OR^{22} , where R^{22} is as defined above *mutatis mutandis*.

65. A polymer according to claim 64 in which Y^2 is $H_2C=CR^{19}COA-$, in which R^{12} is hydrogen or methyl and A is $-O-$ or $-NH-$, B^2 is straight chain C_{2-6} alkanediyl group and Q is $-N^+R^{22}_3$ where each R^{22} group is a C_{1-4} alkyl group.

66. A film formed of a polymer formed by radical polymerisation of ethylenically unsaturated monomers, in which the monomers comprise:

- i) 0.1 to 25 weight% of an ammonium phosphate ester zwitterionic monomer;
- ii) 0.1 to 25 weight% of a zwitterionic comonomer different said ammonium phosphate ester zwitterionic monomer; and
- iii) 25 to 99% of a hydrophobic monomer.

67. A medical device having at least one surface provided with a coating comprising a film formed of a polymer formed by radical polymerisation of ethylenically unsaturated monomers, in which the monomers comprise:

- i) 0.1 to 25 weight% of an ammonium phosphate ester zwitterionic monomer;
- ii) 0.1 to 25 weight% of a zwitterionic comonomer different said ammonium phosphate ester zwitterionic monomer; and
- iii) 25 to 99% of a hydrophobic monomer.